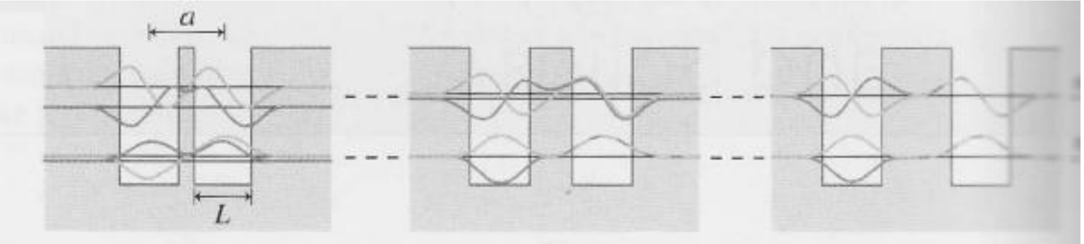
PH102, 2012W, Lecture Notes: February 13, Mon, Class 14

Molecular Bonding

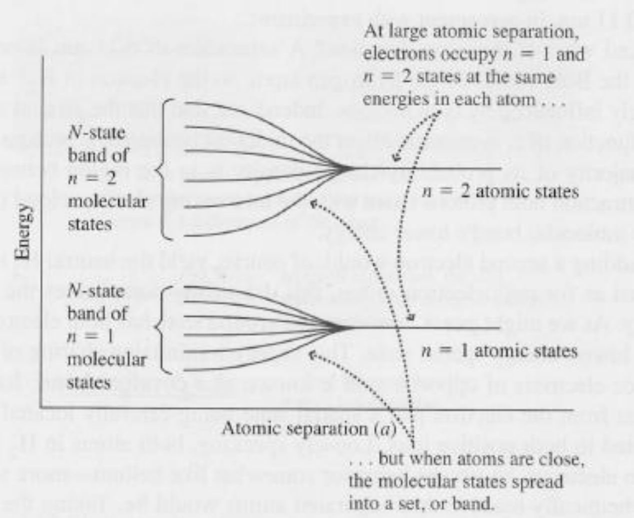
- It is impossible to solve the Schrodinger equation for multi-atom bonding cases. Approximations and qualitative judgments that agree with experimental results are needed to approach the multi-atom bonding situations.
- Two approaches
    - Valence-bond approach: Each shared pair of electrons is represented either by two dots or by a dash between the atoms bonded by them. A molecule consists of individual atoms held together by covalent bonds. Each covalent bond consists of two electrons of opposite spins, each electron is provided by an atom in the molecule. Electrons from each atom in the molecule can be available according to the Hund’s rule where electrons in an atom have parallel spin arrangements which are more stable. E.g. H-H, O=O, N≡N
    - Molecular orbital approach: A molecule is regarded as a single entity and outmost electrons of the molecule participate in bonding atoms together. Orbitals belong to the entire molecule rather than individual atoms. Atoms are held together in a molecule because electrons’ charge distribution is concentrated between the atomic nuclei. Such bond is called covalent bond where electrons have opposite spins allowing spatial part of the wave functions of electrons to be centrally located so that they can be attracted by positive charges of both nuclei.
    - In both approaches, only the valence electrons are considered to participate in bonding because (1) inner electrons are more tightly bound to the nuclei and thus less responsive and (2) repulsive force between atoms becomes predominant at the region where inner electrons mostly reside.

Atoms Come Close to One Another

- A model using two finite potential wells, each of which approximately represents a potential of an atom that an electron experiences

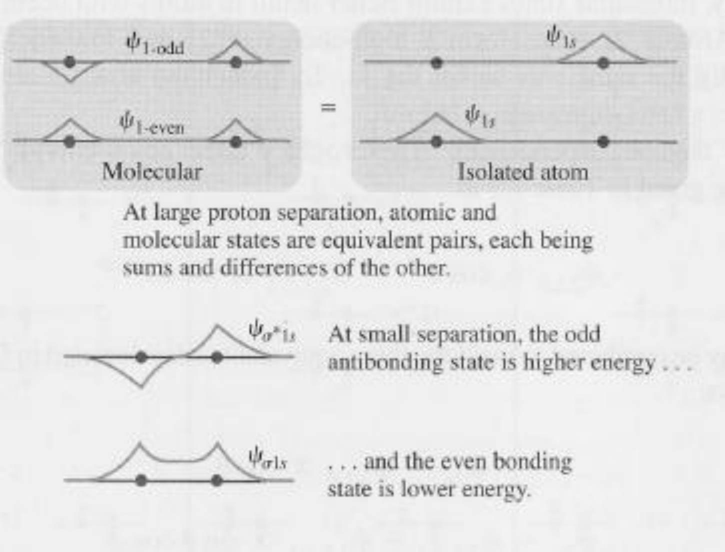


- When N atoms get close enough, each atomic energy level will split into multiple (N) molecular energy levels for an electron to occupy.



Molecules

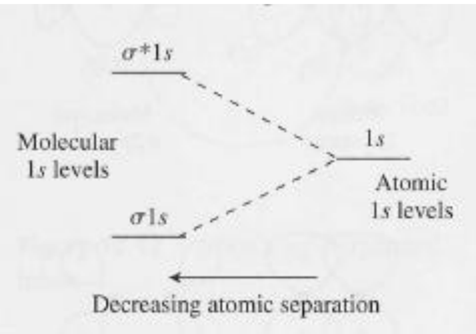
- Atoms form molecules when the molecular state is of lower energy than the separated atoms.
- Electrons can be shared by both atoms in two ways:
    - Bonding state: this lowers energy from the individual atomic energy state
    - Antibonding state: this increases energy from the individual atomic energy state



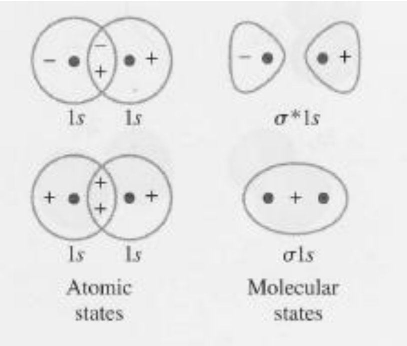
At large proton separation, atomic and molecular states are equivalent pairs, each being sums and differences of the other.

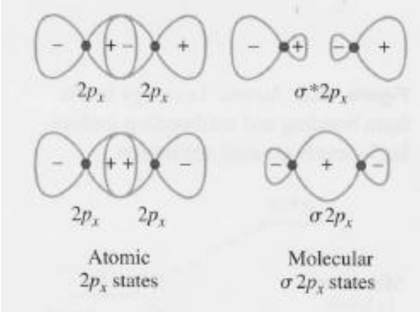
At small separation, the odd antibonding state is higher energy . . .

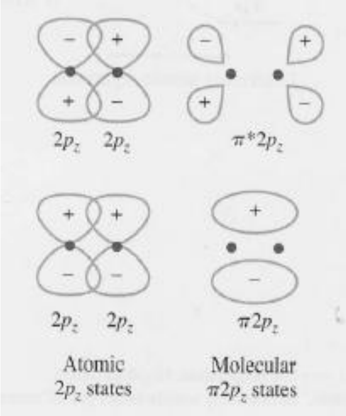
. . . and the even bonding state is lower energy.



- There are different types of molecular orbitals:
    - Sigma orbital (σ): charge density is largest along the molecular axis
        - two 1s orbitals bonding/antibonding → $\sigma 1s$ / $\sigma^* 1s$
        - Two $p_x$orbitals bonding/antibonding (when x is the molecular axis) → $\sigma 2p_x/\sigma^* 2p_x$
    - Pi orbital (π): charge density is largest off the molecular axis
        - off axis p_y orbitals bond/antibond →$\pi 2p_y$/ $\pi^* 2p_y$
- When bonding/anti-bonding states are created for molecular orbitals, atomic orbitals that are orthogonal to each other do not form bonding/anti-bonding molecular orbitals. That is no bonding/antibonding between $p_x$and p_y; $p_y$and p_z; $p_x$and p_z.







- In the molecular orbital approach, we use orbitals created by bonding and antibonding states of atomic orbitals to arrange electrons.

Figure 10.7 Filling of the 1*s* levels in molecular hydrogen and helium.

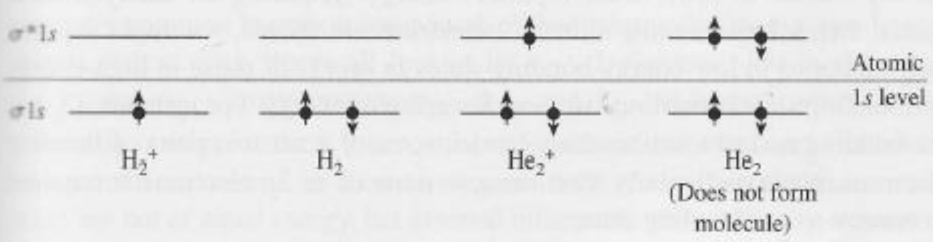
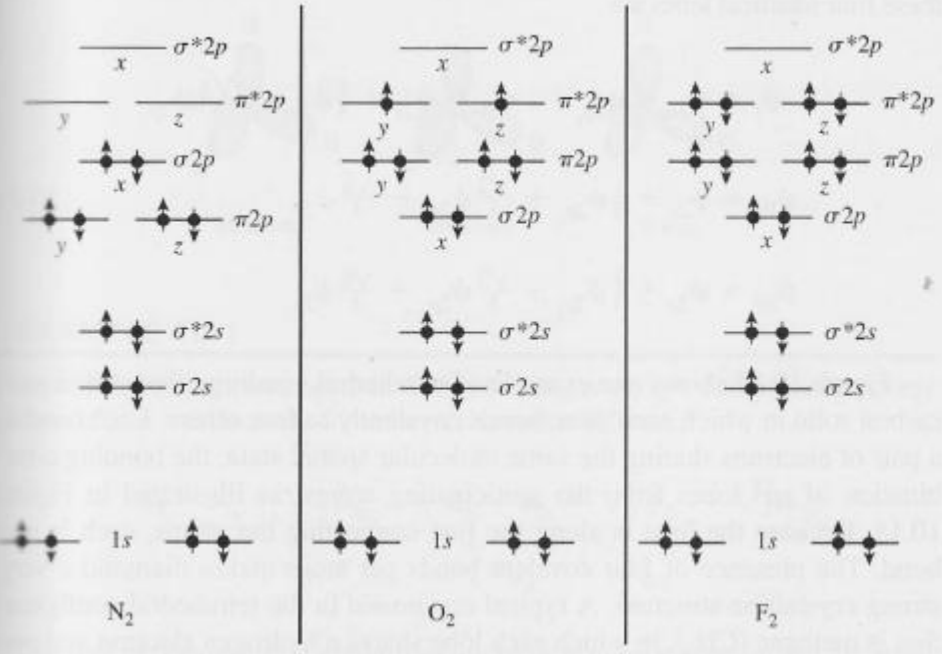
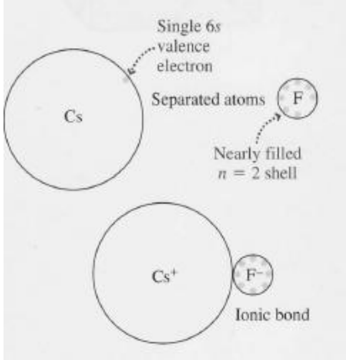


Figure 10.10 Molecular energy levels in nitrogen, oxygen, and fluorine.



  - Inner electrons (1s electrons) are confined to atomic orbitals.
  - The ordering of molecular orbitals varies from element to element.
  - Electrons spread over the degenerate molecular orbitals when possible.
  - Net bonds = ½ (the number of electrons in bonding states – that of electrons in anti-bonding states).
  - The net lowering of energy is contributed by the electrons in the bonding states in excess of those in the antibonding states. Therefore, N_2 is stable than O_2 or F_2.
- Diatomic molecules do not have electric dipole moment because they are symmetric. However, molecules consisting of two different elements can create asymmetric distribution of electric charges, creating polar covalent bonds.

- Ionic Bond occurs when an atom grabs an electron from the other atom and the bond between the two atoms is due to Coulomb interactions.



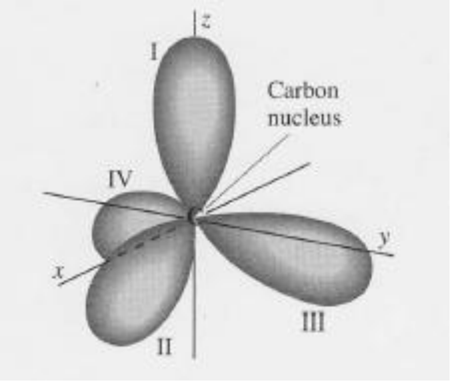
- Hybridized orbital-sp^3: Carbon sometimes share all four n=2 electrons with other atoms creating sp^3 hybridized orbital with the following geometry:

$$\psi_I = \psi_{2s} - \psi_{2p_z}$$

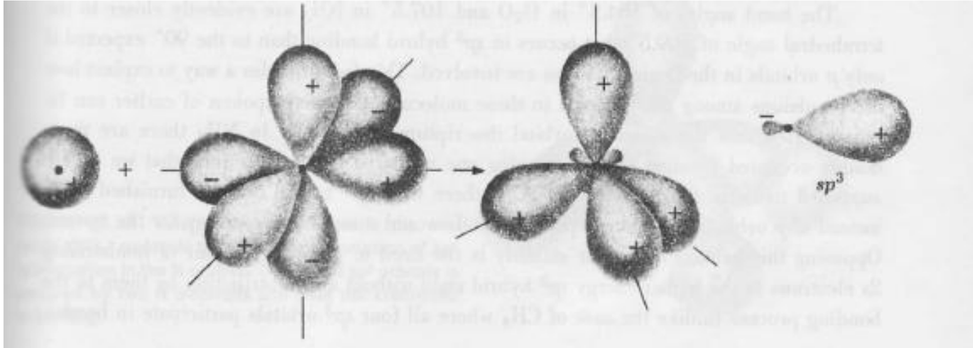
$$\psi_{II} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} - \frac{\sqrt{8}}{3}\psi_{2p_z}$$

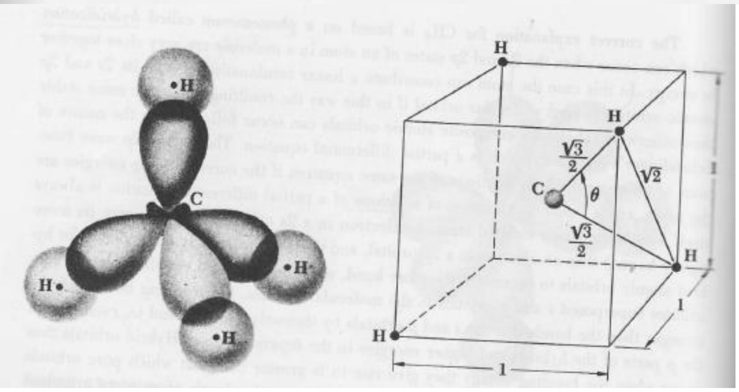
$$\psi_{III} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} + \frac{\sqrt{2}}{3}\psi_{2p_x} - \frac{\sqrt{6}}{3}\psi_{2p_y}$$

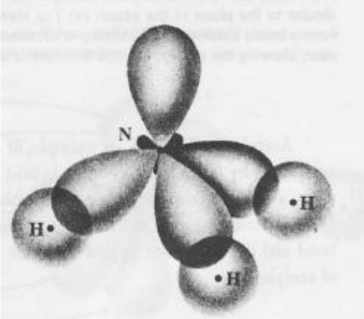
$$\psi_{IV} = \psi_{2s} + \frac{1}{3}\psi_{2p_z} + \frac{\sqrt{2}}{3}\psi_{2p_x} + \frac{\sqrt{6}}{3}\psi_{2p_y}$$



These four lobes are available for σ bonding between electrons. Diamond has this structure, resulting in a very strong structure.







$$\theta = 109.5\,°$$

- Hybridized orbital-sp^2 can be seen in $C_2H_{4.}$ The sp2 orbital is placed on a plane and have 120 degrees between two lobes. p_z orbital is perpendicular to the plane.

$$\psi_I = \psi_{2s} + \sqrt{2}\psi_{2p_x}$$

$$\psi_{II} = \psi_{2s} - \sqrt{\frac{1}{2}}\psi_{2p_x} + \sqrt{\frac{3}{2}}\psi_{2p_y}$$

$$\psi_{II} = \psi_{2s} - \sqrt{\frac{1}{2}}\psi_{2p_x} - \sqrt{\frac{3}{2}}\psi_{2p_y}$$